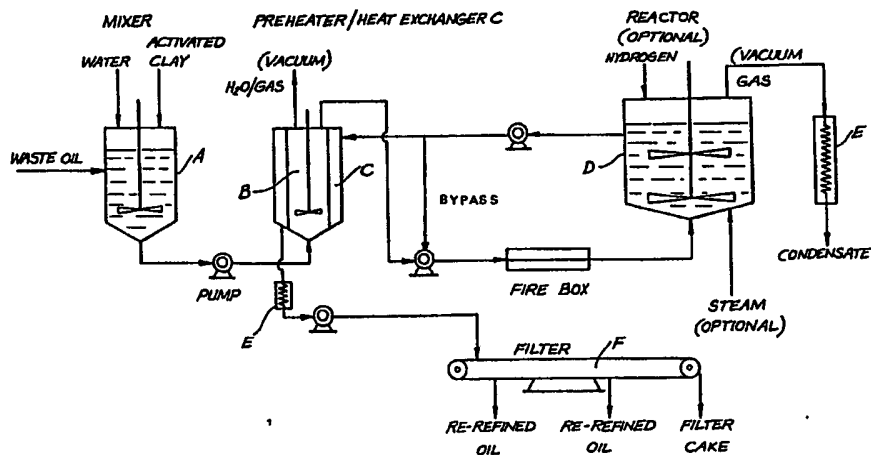




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(54) Title: CONTAMINANTS REMOVAL FROM USED LUBRICATING OIL



(57) Abstract

A process is used to re-refine used lubricating oil for reuse as high quality lubricants comprising: a) mixing oil with a catalyst containing an inorganic compound and acid activated clay of montmorillonite type followed by heating and agitating for a specified temperature and residence time to effect selective cracking of the mixture, b) decreasing the temperature and maintaining agitation for a sufficient time to complete the reaction, c) cooling and filtering the residue to separate clean oil from the mixture. An oil additive comprising inorganic compounds and clays for rendering contaminants inactive is also disclosed.

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CONTAMINANTS REMOVAL FROM USED LUBRICATING OIL

TECHNICAL FIELD

The invention relates to a one step process for removing contaminants from used lubricating oil. More particularly the invention involves contacting the used oil with a pre treatment chemical and clay at elevated temperature and thereafter filtering the treated used oil to remove essentially all the contaminants.

BACKGROUND ART

Used lubricating oils are renewable resources that should be recycled to preserve natural resources and avoid contamination of the environment.

Waste lubricating oils include used motor oil, diesel oil, crankcase oil, transmission oil, and the like, usually collected from gasoline service stations. These waste oils contain a number of contaminants arising both from their use and from additives added prior to their use. These contaminants, for the most part, include calcium, barium, zinc, aluminium and phosphorus arising from detergent dispersant agents, iron from engine wear, lead and light end hydrocarbons from gasoline, and water. In order to reuse these oils, the contaminants must be substantially removed.

Due to the high viscosity of the oil, the fine colloidal or dissolved form the contaminants and the dispersing nature of the additives, the contaminants cannot be removed by a simple filtration procedure without some preliminary treatment.

Various techniques have been used to re-refine the used oils. Modern facilities in the United States have selected distillation and hydro treating processes (e.g. NL 83 04023, US 4 342 645 and 79-34617B). It normally requires large capital investment (i.e. \$20M) which is prohibitive for most small capacity operators. Collection of the used oils for such a large quantity could be difficult for remote areas also.

Conventionally, waste oils are treated in a process which includes metals removal steps, which steps involve coagulating or precipitating the contaminants and thereafter either filtering the oil or removing the metals in an aqueous phase. Often the oil is then clay contacted to remove further colour bodies or metals remaining after the initial metals removal.

One of the most widely used metal removal steps is the acid-clay process. In this process, the light ends are first removed from the oil by steam stripping at a temperature in the range of about 260-345°C. The oil is then contacted with high strength sulfuric acid to precipitate contaminants into the aqueous phase; the contaminants are then removed as an acid sludge. The remaining acidic oil product is thereafter contacted with clay at a temperature in the range of about 149-315°C. to absorb additional contaminants and colour bodies.

There are a number of problems associated with this acid-clay process. Firstly, the process produces large amounts of acid sludge which must be disposed of. Secondly, large volumes of corrosive acid are consumed by the process. Thirdly, up to 20% of the original waste oil is lost with the acid sludge.

Heretofore, the standard practice in this art has involved removing the majority of the contaminants (as by acid contacting), prior to contacting the oil with clay, since it is commonly accepted that the detergent dispersant agents present in the oil rendered the clay-oil mixture unfilterable. Further, high temperature treatments have been avoided when reprocessing waste lubricating oil, to avoid undue cracking of the oil.

Furthermore, the primary step in the use of sulfuric acid for removing metals and other impurities from the used oils, requires removal of water contained in the as collected used oil as it would react with sulfuric acid causing violent reactions. In general, the amount of sulfuric acid required for this type of process varies from 4-10% of dry oil depending on the amount of additives used for blending the virgin oil prior to use and the amount of impurity in the used oils. The higher amount the impurity and the additives the more acid is required, and the higher the loss of used oils as acid sludge. Normally, the amount of acid sludge produced is twice the volume of the acid used. After removing the acid sludge by settlement and decantation, normally 24-72 hours, the oils remaining are treated with clay at 250-300°C for further removal of impurities and colour improvement. The amount of clay used varies from 2-10% depending on the activity and capacity of the clay.

Due to the growing concern for environment and the increased cost to safely dispose the acid sludge, new improved processes have been proposed to reduce the use of sulfuric acid. Wiped film evaporator (NL 83 04023) along with high temperature thermal cracking stage (300-350°C) reactors (DE 3 023 374 C2) have been used to different degrees of success to remove part of the impurity and additives from the used oils. The pretreated oil still requires post-treatment with the sulfuric acid and clay to improve its colour and quality for use as lubricants. The amount of acid has been normally reduced to the 2-7% range but total elimination of the sulfuric acid pre treatment step has not been accomplished along with the need of the clay which normally varied from 2-10%. The amount of clay required depends on its acidity and activity. Normally when acid activated clay is used the amount is lower. However, when neutral clay which has not been acid activated, some residual acid is purposely carried over from the previous acid treatment stage or some additional acid is added to activate the clay in situ. Nonetheless, the temperature of the clay treatment is normally maintained at 250-300°C to avoid undue cracking of the oil.

Other methods have been proposed for reprocessing waste oil by obtaining a metathesis reaction with the contaminants by adding an aqueous solution of pre treatment chemicals, which precipitates the metals to render them phase separable from the oil. In U.S. Patent No. 3 930 988 waste oil is contacted with an aqueous solution of ammonium sulfate and/or ammonium bisulfate to precipitate the metals into an aqueous phase, separable from the oil base. In U.S. Patent No. 3 879 282, waste oil is

contacted with an aqueous solution of one or more of triammonium phosphate, diammonium hydrogen phosphate, and ammonium dihydrogen phosphate. In U.S. Patent No. 4 204 946 waste oil is contacted with an aqueous solution of ammonium sulfate and aluminium sulfate. In all of the above processes, the pre treatment
5 chemicals are added to the waste oil in an aqueous solution and the metals are separated in an aqueous phase. Also, the temperature of the reaction is limited to about 90°-260°C. High temperature treatments have generally been avoided when reprocessing waste lubricating oils to avoid cracking of the oil.

In U.S. Patent No. 4 151 072, a process is described for reprocessing waste oil
10 wherein the oil is contacted with an aqueous solution of an ammonium salt such as ammonium phosphate. The temperature of the oil is raised gradually through one or more contacting vessels to a final temperature of less than about 200°C. to initially achieve a phosphate replacement reaction with the contaminants, and to remove water and light hydrocarbons. The oil is then filtered using a filter aid. It should be noted
15 that the above process again requires that the pre treatment chemicals be added in an aqueous phase, and the temperature of reaction be limited to about 60°-200°C.

In U.S. Patent No. 4 411 774, a waste lubricating oil is contacted with one or more of the pre treatment chemicals selected from the group consisting of ammonium sulfate, ammonium bisulfate, diammonium phosphate, ammonium dihydrogen
20 phosphate, calcium hydrogen phosphate, phosphoric acid, calcium sulfate, aluminium sulfate, sodium sulfate, and magnesium sulfate. The contacting step is performed at a temperature of at least about 345°C. This high temperature of at least about 345°C. is used to ensure removal of light hydrocarbon ends from the waste oil. Lubricating oils generally are defined as having a boiling point above at least about 345°C. The oil
25 mixture is thereafter filtered to obtain a filtrate product reduced in contaminant content. The pre treatment chemical is preferably added to waste oil in the absence of water.

Note that the required pre treatment chemicals to be used in the invention is relatively high varying from 1-5%. It is noted that when large amounts of it is used, substantial amount of SO_x in the gaseous effluent is also generated causing
30 environmental concern. Furthermore, the pretreated used oil must be filtered (causing a yield loss) and post treated with clay or the hydro treating steps to improve its colour and quality.

In U.S. Patent No. 4 383 915 untreated waste lubricating oil, containing detergent dispersant agents, is contacted with decolourising clay and heated for a specified time at
35 a specified temperature with the result that the so-treated oil-clay mixture may thereafter be directly and successfully cooled and filtered to remove contaminants with the solids and yield a useable oil product. More particularly, in the heating step the mixture is maintained at temperature(s) in the range of about 345°-385°C. for a period

of time sufficient to render the mixture amenable to filtration at viable rates. That is, the mixture is readily filterable. For example, if a 500mL sample of oil-clay mixture is held at 345°C for 3-4 hours and then cooled to a conventional filtering temperature, such as 175°C, when filtered under a vacuum of 10mm Hg, using No. 1 Whatman
5 filter paper, the mixture will successfully filter in less than 30 minutes.

Again, the filtered oil product needs further conventional upgrading processes including hydro treating, vacuum distillation and acid-clay contacting. Alternatively, it is useful as is in non-critical circumstances, such as lubrication of railroad cars.

The clay amount used in the pre treatment process is limited to 2-6% by wt. and
10 the oil mixture is heated to 340-360°C for about 1-2 hours. Quantity of clay larger than 6% is not normally recommended due oil loss in the clay. Temperature higher than 360°C is also not normally recommended due to over cracking of oil at such high temperatures.

DISCLOSURE OF THE INVENTION

15 According to the first embodiment of the present invention there is provided a process for the removal of contaminants from used lubricating oil, comprising (a) contacting the oil with catalysts containing inorganic compounds and clays and agitating and heating the resultant mixture so as to effect the selective cracking of said mixture; (b) decreasing the temperature and maintaining agitation for a time sufficient to
20 complete the reaction; and (c) cooling and removing the residue from said mixture.

According to a second embodiment of the present invention there is provided an oil additive for rendering contaminants in used lubricating oil inactive comprising inorganic compounds and clays.

According to a third embodiment of the present invention there is provided an oil
25 whenever produced by the process of this invention.

It has been found that a previously untreated used lubricating oil, containing detergent dispersant agents, may be contacted with pre treatment chemical (catalyst) and acid activated clay in one single reactor heated for a specified time at a specified temperature with the result that the so-treated oil-clay mixture may thereafter be
30 directly and successfully cooled and filtered to remove essentially all the contaminants with the solids and yield a light colour oil directly suitable for reblending with additives prior to cense as lubricants. The ratio of the catalyst and clay used could vary over a large range. Generally speaking, the higher amount of catalyst used the lower amount of clay is required, and the reverse is true also. For example, in an experiment using
35 2.4% catalyst about 8.8% clay is required based on oil to effect a clear separation, while when 0.1% catalyst is used about 12.5% clay is required. It has also been surprisingly found that when higher than 12.5-15% acid activated clay is used no additional chemicals are needed to effect the separation. No over cracking of oil results

provided the process steps described below are strictly followed. However, the ratio of the catalyst and the clay should be controlled to optimise the formation of SO_x by product in the effluent and oil loss in the clay. It is preferred that the amount of the catalyst and the acid activated clay be used in the range of less than 1-2% and 4-15%, respectively.

It is important to control the heating steps very carefully. No clear separation could be obtained at low temperatures. However prolonged heating at high temperature causes undue over cracking. It is found that in the heating step, when the mixture is maintained at temperature(s) in the range about 340-380°C for a short period of time no more than 5-20 minutes, followed by a heating at a substantially lower temperature of 290-335°C for 1-4 hours, best results are obtained tendering the treated mixture readily filterable and with good colour quality suitable for direct additive blending.

Apparently the chemical and the clay work together very rapidly and effectively as catalyst at the high temperature selected altering the dispersing properties while achieving selective cracking of the detergent dispersing agents and other additives associated with the oil. The longer residence time at the lower temperatures allow sufficient time for the reactions to complete without causing undue cracking of the oil. Since there is no over cracking and further removal of acid sludge nor filtration intermediate stages to remove sulfated or phosphated compound sludges from the treated oil and the selective cracking of the additives (i.e. organic and inorganic long chain polymers) have increased the yield of the treated oil, which is normally 5-20% higher than that previously achieved with the conventional system. This is surprising and is in contrast to the teachings of the prior art requiring multi-steps to produce similar quality products.

It is also found that in contrast to the previous observation, water is essential for effective use of the combination of catalyst and clay. In experiments where water is removed from the used oil the proposed system does not seem to be effective. Furthermore, when the clay is predried to remove the water, no separation is effected either. After water is added to the system clear separation is obtained. Apparently water helps to disperse the detergent for the catalyst and clay to work effectively. Water normally exists in the untreated used oil in the range of 4-10%. Steam could also act as a dispersing agent to enhance the stripping of light ends from the treated oil.

BRIEF DESCRIPTION OF DRAWING

Fig. 1 depicts a flow diagram depicting the process of the present invention.

BEST MODE AND OTHER MODES FOR CARRYING OUT THE INVENTION

The concept discussed below is a continuous process which uses an active clay system that eliminates the need of sulfuric acid treatment and produces a clean oil for re-use. The used oil to be processed could be any black oil as is normally understood

or any white oil that has been substantially contaminated. The clay could be F-30 from Engelhard or any other clay that possesses similar properties. The process could include a mixer (A), a preheater (B), a heater exchanger (C), a continuous (stirred tank) reactor (D) a condenser (E), and a continuous or a semi-batch filter (F) as depicted in
5 Figure 1.

The used oil is fed continuously from the storage tank into the mixer where the clay is uniformly mixed with the used oil and preheated before being fed into the bottom of the continuous stirred tank reactor at a specified temperature. The used oil would have a specified residence time (1-4 hours) in the reactor while being discharged
10 continuously from the top of the reactor. The reaction temperature of the reactor should be high enough to finish cracking of the detergent or other additives in the used oil. Temperature required before entering the reactor at 300-350°C must be preheated to 320-380°C for sufficient time (5-20min.) to affect cracking of the detergent and other additive. The processed oil discharged from the reactor is cooled and fed into a
15 continuous belt filter or a semi-batch type filter to separate the clean oil from the used clay.

Alternatively, the used oil could be demetallized using for example the Diammonium phosphate (i.e. Philips process) prior to entering into the clay mixer. The purpose is to avoid metal deposition on the clay. The subsequent process scheme
20 could be the same as without the demetallization step discussed above.

The process could either be practiced batchwise, semi-batchwise or continuously, depending on the plant capacity and economics preference. Since there is no acid pre treatment step required, no acid sludge settlement tanks and sealed transfer lines are required, and there is no down time required for settlement of the acid sludge either.
25 Therefore, even with batch operation, one operation cycle would normally require less than 4-5 hours which is equivalent to 1/3 to 1/4 the time required for the conventional contacting process not counting the acid pre treatment time. Furthermore, significantly less land is required favouring tight space operation capability. The new process, therefore, provides savings in capital and operating expenses.

The as collected oil normally contains 4-10% water which does not require preliminary removal beforehand. Preferably some water (up to 5%) is added if the total initial water content is less than 4%. The used oil is preferably treated directly by the present process without preliminary light ends stripping. Since the contacting step of the process utilises a high temperature, light ends stripping is conveniently
30 performed simultaneously with this step. Alternatively the process may be practised with a preliminary, intermediate or final light ends stripping step. The stripping could be either conducted by slight vacuum to effect distillation or by supersaturated steam. With proper stripping the colour and smell of the oil product has improved colour.

Used oil prepared by preliminary thermal cracking steps seems to be more difficult to treat using the present invention probably due to clay fouling. The clay contacting step could also be performed in a hydrogen atmosphere. Improvements in the odour of the oil could be obtained due to the hydrogenation of S-containing compounds.

5 The catalyst added to the acid activated clays and the oil mixture could be in either aqueous form or dry form containing phosphate sulfate and/or chloride cations. They can also be pre blended with acid activated clay before being mixed in the clay treaters. The catalyst amount required is normally no more than 2% and is preferably less than 1%. The clay preferred is acid activated (and acid activatable) montmorillonite
10 type bentonites. The acid activated clay may be activated by any suitable acid known in the art, for example sulfuric acid or hydrochloric acid. When neutral clay unactivated by acid is used, generally sulfuric acid could be used proportionately to activate the clay in-situ inside the same reactors at lower temperatures before the final reactor temperature is reached.

15 The used oil after preheating to 200-250°C is preferably heated subsequently in a direct fired heat box to reach a maximum temperature of 340-380°C to effect the selective cracking of impurities and additives. The residence time in the maximum temperature is to be no more than 20 minutes and preferably 5-10min. Too long a residence time under the maximum temperature could cause undue cracking of oil. The
20 high temperature treated oil entering into the continuous recycled or stirred tank reactor is preferably kept for a residence time of 1-2 hours and no more than 4 hours to ensure completion of the reactions. The finished used oil mixture is then circulated to the preheater for preliminary cooling before it is finally cooled in a heat exchanger to 100-150°C before filtration. The gaseous product produced from the clay reactor can be
25 condensed and fractionated to produce various distillate products as the conventional process. The treated oil after filtration has colours ranging from 1.5-4 depending on the colour specification required. Generally the lower the colour the higher the catalyst or clay loading is required, but normally no more than 15% clay is required for an ASTM colour of 1.5-3. The preferred clay loading is in the range 5-12.5% by wt of
30 the used oil. Lower than 5% the colour of the product oil could be too dark. While higher than or equal to 12.5% clay is used, a strong acidic clay could effect the cracking of the additives to produce clean oil product without added catalyst. However, contrary to the previous teaching (US Patent 4 411 774) Attapulugus clay and other Fuller's Earth clay which could not be easily acid activated are found to be
35 ineffective for this purpose. Oil retention on the clay is also found small due to the high filterability of the treated oil. The used clay after filtration is generally neutral in acidity and would not further neutralisation treating steps.

The present invention will now be described with reference to the following

examples which should not be construed as limiting on the scope thereof.

EXAMPLE 1

Tests to confirm the effectiveness of the present invention.

EXPERIMENTAL

5 1. Materials

1.1 Oils

Three used crankcase oils were subjected to re-refining in this investigation. These oils, their sources and descriptions were as follows:

Oil No.1 From 16th & MacDonald Chevron, 3250 MacDonald St., Vancouver,
10 B.C.: mixture of crankcase and gear oils.

Oil No. 2 From Dunbar Shell Service, 4195 Dunbar Street, Vancouver, B.C.:
crankcase oil from single car receiving service.

Oil No. 3 From Delta Truck Repair Ltd., 7731 Vantage Way, Ladner, B.C.:
crankcase oil from diesel powered trucks.

15 1.2 Catalyst System

The three catalyst components are understood to have been purchased from Van Waters & Rogers Ltd., Richmond, B.C. by Hy Pow'r.

2 Refining Methods

Preparation of Samples for Analysis

20 Initially (Runs 1 to 6) a 1L 3-neck flask fitted with a stirrer, thermometer and distillation take-off head plus condenser and receiver was used to treat used oil with catalyst. The apparatus was heated to temperature using an electrically heated mantle. The D-shaped Teflon plastic stirrer blade used was capable of sweeping approximately 80cm² of the flask bottom, an area sufficient to agitate the entire amount of catalyst and
25 clay. The rate of agitation was approximately 60rpm. Later experiments (Runs 7 to 9) employed a 2L 3-neck flask with the same accessories. The use of a larger flask was necessary in order to accommodate the large volume of foam generated during the reaction process.

Typically, weighed quantities of used oil (usually 250g), the catalyst mixture
30 (usually 6g), and clay (usually 22g) were introduced into the flask. The stirrer was then started, the heat applied via a variable transformer and the rise in temperature with time noted. When the temperature reached 130°C and water and gasoline were being distilled from the oil, the rate of temperature rise was usually adjusted to accommodate foaming. This was necessary in order to prevent loss of oil through the distillation head
35 and into the receiver. At ~150 to 160°C when foaming had ceased, the rate of temperature rise could then be increased until it reached the maximum which was in the region of 345 to 360°C.

Following a period at maximum temperature, during which time coagulation

usually took place, the oil was allowed to slowly cool in air to approximately 150°C after which the flask was cooled in cold water. The oil at room temperature was then separated from the catalyst and clay by means of vacuum assisted filtration through a Whatman No. 1 cellulose filter paper using a Buchner flask and filter funnel. The weight of oil passing the filter, the combined weights of clay, sludge, catalyst and entrained oil were then determined.

2.2 Investigation of Various Catalyst Systems

In order to rapidly screen the effectiveness of various ratios of the three catalyst components and clay, oil and the different catalyst/clay mixtures were simply heated using a hot plate to the required temperatures in Erlenmeyer flasks while being stirred magnetically. After cooling, the mixtures were inspected visually to determine whether coagulation had taken place. They were then filtered as before. No yield or analytical data was gathered in these tests.

3 Analytical Methods

Following separation of spent catalyst and clay in Section 4.2.1, re-refined oils produced in runs where foaming had not caused loss of product were despatched to Preventative Maintenance Methods Ltd. for examination. The following analyses and properties were determined:

Metals: Iron, chromium, copper, lead, aluminium, tin, sodium, magnesium, silver nickel, zinc calcium, plus silicon (a non-metal).

Neutralisation Number (unrefined oil only)

Acid Number (re-refined oil only)

Flash point (Cleveland Closed Cup, re-refined oil only)

Bottom sediment and water (BS & W)

Viscosities at 40° and 100°C (re-refined oils only).

Solids including catalyst, clay, coagulated oil impurities and entrained re-refined oil were analysed at B.C. Research for zinc and lead. the procedure involved ashing the material removed from the oil by filtration at 800°C, digesting the residues with 50X nitric acid, filtering off insolubles, diluting to known volume and measuring the metal contents by atomic absorption spectrophotometry (AA).

RESULTS AND DISCUSSION

Table 1 summarises data gathered in 9 separate experiments where different used oils were treated with the standard Hy Pow'r catalyst consisting of equal quantities of the three catalyst components. Attempts to gather quantitative yield data were frustrated initially by the excessive foaming which occurred between ~120 and 170°C. This resulted in losses of oil through physical carry over with distillate. However, provided the catalyst level was kept at approximately 6% on the weight of oil, clarification was achieved when the temperature was raised in excess of 345°C (Run 2). In other words,

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initial experiments indicated that the process worked, but they yielded no quantitative information. The fact that a combination of 0.1X catalyst and 10X clay on oil weight did not result in oil clarification (Run 1) when this mixture was found to clarify oil in Hy Pow'r's plant can possibly be explained, as follows: In the plant, the pump used to
5 circulate the oil-catalyst slurry through the heat exchanger to the reactor probably subjects the mixture to greater shear action than the stirrer used in the laboratory. In the plant, the oil catalyst mixtures experienced longer periods at the elevated temperatures than in the laboratory experiments. The combination of high shear and sustained high temperatures are believed to make an important contribution to the success of the
10 clarification process. They allow smaller quantities of catalyst and clay to be employed using the plant equipment than is possible in the laboratory. This of course has a significant positive effect on the economics of the Hy Pow'r process.

When foaming was eliminated by drying the catalyst and clay on the one hand, and by prior removal of water from the oil by distillation, on the other, no clarification
15 was achieved even when the final temperature was raised to 350°C (Runs 4 & S). Addition of water to a mixture which had not clarified initially, followed by reheating, re-introduced the foaming problem, but now resulted in clarification (Run 4A).

When the foaming was recognised as an important part of the process, a large flask was used to accommodate the 600-700X increase on oil volume of this foam.
20 After this change, quantitative yield data became available. Runs 7, 8 and 9 on different oils showed that yields of re-refined oil of up to 70X based on used oil were attainable. This was possible even using a relatively inefficient laboratory vacuum filtration system. Yields in excess of this are thought to be easily attainable if a pressure filter system (or centrifuge) had been available to separate clay and catalyst from the clarified
25 oil. In the laboratory, vacuum filtration only allows a maximum of 14 pounds per square inch pressure to be placed on the filter pad. Greater pressure differentials would permit greater recovery of oil from the pad. The percentage of total material (oil, catalyst, clay) entering the re-refining system that can be accounted for in re-refined products, liquid distillate fraction and solids retained on the filter pad, but excluding
30 non condensable gases (i.e. the mass balance), ranges from 98 to 100X for Runs 7, 8 and 9. This indicates that few or no mechanical or handling losses occurred during the experiments. Table 1 shows that the three different used oils all respond to treatment with the Hy Pow'r catalyst system. These oils foamed to different degrees and some produced oxides of nitrogen and elemental sulfur which came over with the distillate,
35 but all oils examined were clarified by the Hy Pow'r process.

Table 2 summarises the results of treating No. 2 oil with different combinations of the Hy Pow'r catalyst system in conjunction with clay. It will be seen that all catalyst combinations cause clarification of the oil, but the combination which contains equal

amounts of the three ingredients is preferred. This mixture generates the greatest volume of foam. Since this characteristic indicates that the catalyst is causing coagulation of suspended impurities, it is thought that clarification efficiency is related to the foam volume.

5 Table 3 summarises analytical data on both the raw and re-refined oils. The results show that treatment of all three raw oils converts them into clear pale yellow coloured base stocks. Virtually all contaminant metals are removed along with other suspended materials by the Hy Pow'r process. The re-refined oils have low BS & W values and low total acid numbers. The re-refined oil viscosities all correspond to oils
10 with SAE Nos. of 20 with viscosity indices in the range 109 to 180. The flash points of the products examined range from 189 to 218°C.

Table 3 includes lead and zinc levels for the solids recovered on the filter pads. It will be seen that metals removed from the raw oils during treatment are associated with solids removed from re-refined oils by filtration. (No attempts have been made to
15 obtain material balances of metals originally present in the raw oils and subsequently being deposited on the filter pads.

CONCLUSIONS

Laboratory scale tests have shown that the Hy Pow'r Oil & Gas Ltd. catalyst system which consists of equal quantities of the three catalyst components in
20 combination with an appropriate clay is capable of removing virtually all metals and suspended impurities from a variety of used crankcase oils. These tests have also shown that the re-refined oils produced will most likely be suitable base stocks for the production of premium motor oils following the addition of appropriate additive packages. A comparison of the laboratory results with plant experience has indicated
25 that the amount of catalyst and clay required to achieve purification of used oils is dependent upon the intensity of mixing (shear) and the period at elevated temperature. It is believed that the greater shear and longer heat up time experienced in the plant increases catalyst efficiency so that less catalyst than that used in the laboratory experiments is required to achieve oil purification. Any operating cost calculations
30 should therefore use chemical consumption data generated in past plant trials and not quantities used in the laboratory. In addition, any future modifications to the plant should not reduce the shear applied to the oil slurry.

The current investigation has shown that water plays an important role in the process. Should any batch of used oil, because it contains little water, not respond to
35 the new re-refining system, injection of steam into the mixture is likely to assist the clarification step. Furthermore, steam injection could sparge more volatile components from oil and raise the flash points of the final product to above current observed levels of 134-218°C.

- Virtually all metals and suspended oil impurities removed from used oil during the Hy Pow'r re-refining process remain in the solids removed by filtration. Unlike the acid sludge generated by the old acid/clay oil re-refining process, the by products of the Hy Pow'r process should present no difficult disposal problems. Predictably, metals of environmental concern including lead will be significantly less likely to leach from the solid by product mixture entering a landfill disposal site.

EXAMPLE 2

Analysis of waste oil sample.

- | | | |
|----|--|---|
| | Appearance | Clear and bright |
| 10 | Odour | Typical of clay treated re-refined oils |
| | Colour | ASTM D1500 L2 |
| | Viscosity @ 100°C (mm ² /S) | 7.18 |
| | Viscosity @ 40°C (mm ² /S) | 50.5 |
| | VI (Viscosity Index) | 100 |
| 15 | SAE NO | 20 |
| | SSU @ 100°F (Sayboltsec.) | 260 |
| | Flash Point (C.O.C.) | 179°C |
| | Pour Point | -9°C |
| | Acidity (New No.) | 0.01mg KOH/g |
| 20 | Elemental Analysis | Ca < 1ppm |
| | | Mg < 1ppm |
| | | Zn 9ppm |
| | | P < 1ppm |
| | Copper Strip Corrosion | 1 b |
| 25 | Filtration | The oil still contains some clay. The attached filter has been used to filter 100mL of oil. |

COMMENTS:

- To some extent the "quality" of a re-refined base stock is a matter of opinion as there is no universally accepted specification, and it depends on the suitability of the product for its intended use.

It is possible however, to make some comments on how a re-refined product compares with a virgin base oil.

- The general appearance on colour of this product are very good. (Although appearance and colour may not have any technical significance, they certainly affect the marketability of the product.)

The odour is unpleasant and is typical of acid/clay re-refined oils.

The viscosity index of 100 is higher than typical Canadian base stocks and this probably indicates that some viscosity index improvers (polymers) remain in the oil. It

is almost impossible to completely remove these compounds without total distillation. The presence of these compounds are not necessarily harmful.

e.g. a) In formulating multigrade engine oils they would be an advantage in that less VI improver would be needed

5 b) In formulating oils requiring good demulsibility such as turbine oils they would probably be deleterious.

Pour Point is a reasonable figure for base oil

Acidity is very low. It is comparable with the best acid/clay re-refined oils and better than most. It is close to the figure obtained on virgin base stocks.

10 Elemental analysis shows a very good removal of additive metals and contaminants. The only slight remaining material is 9ppm Zinc (down from approximately. 1000ppm in typical used oil).

The cleanliness problem (filtration) is easily remedied by filtering down to 15 microns; preferably using a paper filter.

15 The only superior re-refined oils analysed were all manufactured using a distillation/hydro treating process.

i.e. KTI process used in Greece
Shell/Phillips plant in Toronto

Mohawk Lubricants plant in North Vancouver

20 The flashpoint of a typical virgin SAE 20 base oil is 230C. It would not be reasonable to expect to achieve this sort of figure without fractionation (i.e. prior removal of SAE 5 or SAE 10 oil).

However, the flashpoint of Shell 100 neutral (SAE 5W) oil is 196°C min. as is the Mohawk SAE 10 oil (Mohawk HT 150). The only oil sold in Canada with a
25 flashpoint as low as 179C is Imperial SAE 5W, and the Imperial SAE 10W is 200°C min.

The indications therefore are that fuel removal is incomplete. The possible problems associated with low flashpoint and hence higher volatility are that some engine tests and specifications are difficult to achieve.

30 This however is a criticism of the plant, or of the operation of the plant, rather than a criticism of the process, which appears to produce a very good quality product.

Further examples are given below using "treated acid activated clay" containing 0.1% pre blended catalyst consisting 0.03% each of $MgSO_4$, $Al_2(SO_4)_3$ and NaCl, respectively. The treated clay normally contained about 14-15% moisture. The
35 percentage clay used is based on undried weight and untreated oil basis:

EXAMPLE 3

Raw and re-refined analytical data.

EXAMPLE 4

In the experiment, 1000g of untreated oil was added 10g of water and 200g of "treated acid activated clay" heated in a three neck flask equipped with a stirrer under nitrogen purge to 370°C for 10min. The dark black untreated oil contains 1192, 774, 550, 579, 64, 30, 43, 134, 40, 25, 9, 813 and 400ppm of Ca, Zn, Mg, P, Ba, B, Cu, Fe, Si, Al, Cr, Pb, and Na metal ion impurities. After proper treatment and separation, about 150g water, 136g of gas oil and 734g of lube oil were collected. Therefore, the lube oil yield was about 73% with an ASTM colour of 3-3.5 and a TAN of 0.03. The metal impurities were all reduced to lower than 1 ppm except Ca, Si and Na which were 2.8, 59.8 and 1.2 ppm, respectively.

10

EXAMPLE 5

In the plant experiment, 215 litre of black oil containing 5% water and 12% of the "treated acid activated clay" were added to a stirred metal reactor directly heated from the bottom. Fire was extinguished at 250°C after 2.5 hours and the temperature descended to 230°C after 10min. before the final temperature rose to 340°C in 15-20min. with continuous agitation. The treated oil has a light ASTM colour of 2-2.5 and was easily filtered. The resultant yields for water, light ends and lube oil were about 5, 11 and 72%, respectively. About 8% gaseous product was not condensed due to inefficient condenser system.

15

EXAMPLE 6

In the same plant apparatus described above, 200 litre of black oil was added 12.5 and 13% clay with no additional water. The entire reactor was heated to 360°C for 30min. The recovered lube oil yield after filtration was very low at about 35% yield, while the recovery of light ends and water were approximately 55%, and the non condensable gases were about 10%. Apparently, there was undue over cracking of oil at the prolonged heating of 360°C.

20

25

EXAMPLE 7

The above experiment was repeated with 250 litre of used oil and 11% of the treated clay but heated to 350°C for 20-30min. The lube oil yield was 70% with 2-2.5 ASTM colour.

30

EXAMPLE 8

The above experiment was repeated with 200 litre oil and 20kg treated clay. The fire was extinguished when the temperature reached 260°C. The temperature reached 335-340°C after 1 min. The reactor was cooled and re-heated to 255°C for 30min. The lube oil with an ASTM colour of 2.5-3 obtained has a 80% yield.

35

EXAMPLE 9

Experiment was carried out in a 500 litre reactor equipped with a recirculation loop being heated externally by direct fire. In the experiment 6% water and 15% clay was added to 250 litre oil. The maximum temperature reached in the recirculation loop

15

was 360°C and the residence time was no longer than 5min before entering into the reactor where the temperature was gradually increased to 320°C. The external fire was extinguished after the reactor temperature was kept at 320°C for 20min. The external fire was then distinguished and the reactor was cooled to 165°C before filtration
5 started. The treated oil had a very rapid filtration rate. The lube oil yield was 73% based on dry oil and had an initial colour of 1.5 and 3.5 after 3 days in air. The product oil has the following properties:

Density: 0.8803 g/cc

Viscosity: 35.93 CS (40°C); 6.03 CS (100°C)

10 Viscosity Index: 112

Pour Pt: -12°C

Flash Point: 186°C

IAT, mg KOH/g: 0.04

S % wt: 0.34

15 Zn % wt: ND

Na % wt: ND

EXAMPLE 10

The above experiment was repeated but the recirculation loop temperature never reached higher than 350°C and the reactor temperature was maintained at 340°C for
20 20min. The resultant yield was calculated to be about 74% yield. Even though the product oil was easily filterable the colour was 4-4.5. Apparently the temperature in the recirculation loop was not high enough and the residence time in the reactor was not long enough to allow the separation reactions to complete.

INDUSTRIAL APPLICABILITY

25 It should be clear that the process and product of the present invention will find wide use in the industry.

The foregoing describes only some embodiments of the present invention and modifications obvious to those skilled in the art can be made thereto without departing from the scope of the invention.

TABLE 1
EVALUATION OF HY POW'R OIL & GAS LTD. USED OIL RE-REFINING SYSTEM:
EFFECT OF VARIOUS PROCESS VARIABLES ON YIELD OF OIL & PREPARATION OF SAMPLES FOR ANALYSIS

Run No.	Raw Materials	Oil	Catalyst ¹	Clay	Process Temperature Conditions			Distillate Phases			Filtered Solids Recovered & on Dry Catalyst & Clay (Wt)	Refined Oil Recovered % on Oil (Wt)	Mass Balance (% Material Accounted for)
					Quantity (g)	Ratio of Catalyst	Oil % on Oil	Time to Maximum (min)	Maximum Temperature (°C)	Time at Maximum (min)			
1	1	500	1:1:1	0.1	10	30	360	10	-	-	-	-	-
2	2	250	1:1:1	6	22	30	350	10	-	-	-	-	-
3	2	250	1:1:1	3	11	105	345	10	-	-	-	-	-
4	2	250	1:1:1	6	22	30	350	10	-	-	-	-	-
4a				22	22	30	360	10	-	-	-	-	-
5	2	250	1:1:1	6	22	30	350	10	-	-	-	-	-
6	2	250	1:1:1	6	22	30	350	10	-	-	-	-	-
7	2	250	1:1:1	6	22	30	350	10	-	-	-	-	-
8	1	250	1:1:1	6	22	30	350	10	3.5 (8.7g)	4 (10g)	201 (110g)	70 (175g)	99.7
9	3	250	1:1:1	6	22	30	350	10	4.4 (11g)	7.4 (18.5g)	221 (121g)	59 (148g)	98.1
									8.0 (20g)	6.4 (16g)	191 (104g)	66 (165g)	100

¹Weight applied to 250 g oil = 14.89 (9.7 g dry). Weight clay used 56 g (44.8 g dry)

RUN NO. COMMENTS

- Used 1 L flask. Lost oil due to excessive foaming and oxides of nitrogen evolved at 150°C. Remaining oil did not clarify.
- Lost oil due to foaming at 130°C. Oil did clarify.

- 3 Lost oil due to foaming between 120° and 160°C. Did not clarify.
- 4 Used catalyst and clay pre-dried at 150°C on cooled oil which had also been dried by heating to 160°C in absence of catalyst. No foam following mixing, but no clarification.
- 4a Added 20 ml water to No. 4 run after cooling and reheated. Now foam produced, oil losses but now clarifies.
- 5 Catalyst dissolved in water, mixed with clay, dried at 105°C, ground up added to oil. No foaming, no clarification.
- 6 Clay dried at 105°C, catalyst used as received. Foamed over at "130°C.
- 7 Used 2 L flask to retain foam. Oil clarifies. Some oil left on filter pad. Clarifies. Filters easily. Foam volume 1500 ml.
- 8 As for No. 7. Oxides of nitrogen evolved. Less foam than No. 2 oil. Clarifies slowly. Difficult to filter. Some oil left on filter pad. Foam volume 1200 ml.
- 9 As for No. 7. Sulphur deposited in condenser. Least foam of all oils. Oil clarifies. Slow to filter. Foam volume 700 ml.

TABLE 2

Evaluation of Hy Pow'r Oil & Gas Ltd Used Oil Refining System: Effect of Different Catalyst Component Ratios on Oil Clarification*1					
Run No	Catalyst Ratio		Foaming		Comments
	Component 1	Component 2	Component 3	Temperature Range (°C)	Maximum Volume (mL)
10	1	98	1	100-35	600
11	98	1	1	135-70	400
12	1	1	98	100-40	400
13	33	33	33	135-70	800

*1 100g No. 2 oil treated with 6g hydrated catalyst mixture, 22g of clay. All samples stirred and heated at same rate to 350°C

TABLE 3
PROPERTIES AND ANALYSES OF RAW OILS, OILS RE-REFINED USING HY POW'R OIL & GAS LTD. CATALYST SYSTEM AND SLUDGE BYPRODUCTS

PROPERTY/ANALYSIS		Oil Sample (Run No)				Sludges Derived from Oil No				
		No. 1 (Run 8)		No. 2 (Run 7)		No. 3 (Run 9)		No. 1 (Run 8)	No. 2 (Run 7)	No. 3 (Run 9)
Elements:	Clarity	Raw	Rerefined	Raw	Rerefined	Raw	Rerefined	Raw	Rerefined	
		"Black"	Clear Yellow	"Black"	Clear Yellow	"Black"	Clear Yellow	"Black"	Clear Yellow	
Iron	(pp m)	786	2	324	1			1	1	
Chromium	"	20	1	6	1			1	1	
Copper	"	56	1	32	1			1	1	
Lead	"	900	8	900	44			44	1	1514 2442 269
Aluminium	"	22	1	10	1			1	1	
Silicon	"	13	1	9	1			1	1	
Tin	"	13	1	1	1			1	1	
Sodium	"	125	1	22	1			1	1	
Magnesium	"	884	1	419	1			1	1	
Silver	"	1	1	1	1			1	1	
Nickel	"	4	1	1	1			1	1	
Zinc	"	900	1	815	2			900+	1	375 128 777
Calcium	"	1000+	37	1000+	13			1000+	1	
Total acid number (TAN)			282		1.61				0	
Total base number (TBN)		-3.93		-2.81				-6.73		
Bottom Sediment & Water (BS & W)(%)		2.1	0.1	0.5	0.1			0.5	0.1	
Viscosity at 100°C (centistokes)		-	7.74	-	6.97				6.97	
Viscosity at 40°C (centistokes)		-	53.3	-	24.9				53.4	
Viscosity Index			109		180					
SAE No.		-	20	-	20			-	20	
Flash Point (C.O.C. °F)			424		380				372	

TABLE 4

UNIT NUMBER	IRON	CHROMIUM	COPPER	LEAD	ALUMINUM	SILICON	TIN	SODIUM	MAGNESIUM	SILVER	NICKEL
SAMPLE 1	1	1	1	1	1	1	1	1	1	1	1
SAMPLE 2	1	1	1	44	1	1	1	1	1	1	1
SAMPLE 3	1	1	1	44	1	1	1	1	1	1	1
SAMPLE 4	324	6	32	900	10	9	1	22	419	1	1
SAMPLE 5	2	1	1	8	1	1	1	1	1	1	1
SAMPLE 6	786	20	56	900	22	13	13	125	884	1	4

Sample 1 REFINED. Zinc level is 1 ppm. Calcium level is 1 ppm. Tan = Nil. BS&W = 0.1%. Flash point (C.O.C.) IS 372 F. Viscosity at 40 ° C. is 248.3 (53.4 cst).

Viscosity at 100°C is 49.0 SUS (6.97 cst).

Sample 2 RAW OIL. Zinc level is 900 + ppm. Calcium level is 1000 + ppm. TBN is 6.73. BS&W = 0.5%.

Sample 3 REFINED. Zinc level is 2 ppm. Calcium level is 13 ppm. TAN = 1.61. BS&W = 0.1%. Flash point (C.O.C.) IS 380 F. Viscosity at 40° C is 118.7 SUS (24.9 cst). Viscosity at 100°C. is 39.0 SUS (6.97 cst).

Sample 4 RAW OIL. Zinc level is 815 ppm. Calcium level is 100 + ppm. TBN = 2.81. BS&W = 0.5%.

Sample 5 REFINED. Zinc level is 1 ppm. Calcium level is 37 ppm. TAN = 2.82. BS&W = 0.1%. Flash Point (C.O.C.) = 424 F. Viscosity at 40°C. is 247.9 SUS (53.3 cst). Viscosity at 100°C is 51.5 SUS (7.74 cst).

Sample 6 RAW OIL. Zinc level is 900 + ppm. Calcium level is 1000 + ppm. TBN = 3.93. BS&W = 2.1%.

PROCESS AND PRODUCT**CLAIMS**

1. A process for the removal of contaminants from used lubricating oil, comprising (a) contacting the oil with catalysts containing inorganic compounds and
5 clays and agitating and heating the resultant mixture so as to effect the selective cracking of said mixture; (b) decreasing the temperature and maintaining agitation for a time sufficient to complete the reaction; and (c) cooling and removing the residue from said mixture.
2. The process of claim 1 wherein the used lubricating oil is untreated.
- 10 3. The process of claim 1 or claim 2 wherein the inorganic compound comprises an anion selected from the group consisting of phosphate, sulfate, and chloride; or the product from a reaction giving rise to said anion.
4. The process according to any one of claims 1 to 3 wherein the concentration of inorganic compound is from about 1 to about 98% w/v.
- 15 5. The process according to any one of claims 1 to 4 wherein the inorganic compounds are magnesium sulfate, aluminium sulfate, and sodium chloride.
6. The process according to claim 5 wherein said compounds are present in equal amounts.
7. The process according to any one of claims 1 to 3 wherein the inorganic
20 compounds comprise magnesium sulfate, aluminium sulfate, sodium hydroxide and sodium hypochlorite in the proportion of 2:1:1:1.
8. The process according to any one of claims 1 to 7 wherein the clay is a filter clay.
9. The process according to claim 8 wherein the clay is acid activated.
- 25 10. The process according to any one of claims 1 to 9 wherein the clay is acid activated or acid activatable montmorillonite type bentonite.
11. The process according to any one of claims 1 to 10 wherein the oil:inorganic:clay mixture is heated to 340-380°C.
12. The process according to claim 11 wherein the oil is preheated to 200-
30 250°C.
13. The process according to any one of claims 1 to 12 wherein the residence time of (a) is less than 20 minutes.
14. The process according to claim 13 wherein the residence time is about 5 to 10 minutes.
- 35 15. The process according to any one of claims 1 to 14 wherein the residence time in (b) is less than 4 hours.
16. The process according to claim 15 wherein the residence time is about 1 to 2 hours.

17. The process according to any one of claims 1 to 16 wherein the temperature prior to separation of the residue is lowered to about 100 to 150°C.

18. An oil additive for rendering contaminants in used lubricating oil inactive comprising inorganic compounds and clays.

5 19. The additive according to claim 18 wherein the inorganic compound comprises an anion selected from the group consisting of phosphate, sulfate, and chloride; or the product from a reaction giving rise to said anion.

20. The additive according to claim 18 or claim 19 wherein the concentration of inorganic compound is from about 1 to about 98% w/v.

10 21. The additive according to claim 18 to claim 20 wherein the inorganic compounds are magnesium sulfate, aluminium sulfate, and sodium chloride.

22. The additive according to any one of claims 18 to 21 wherein said compounds are present in equal amounts.

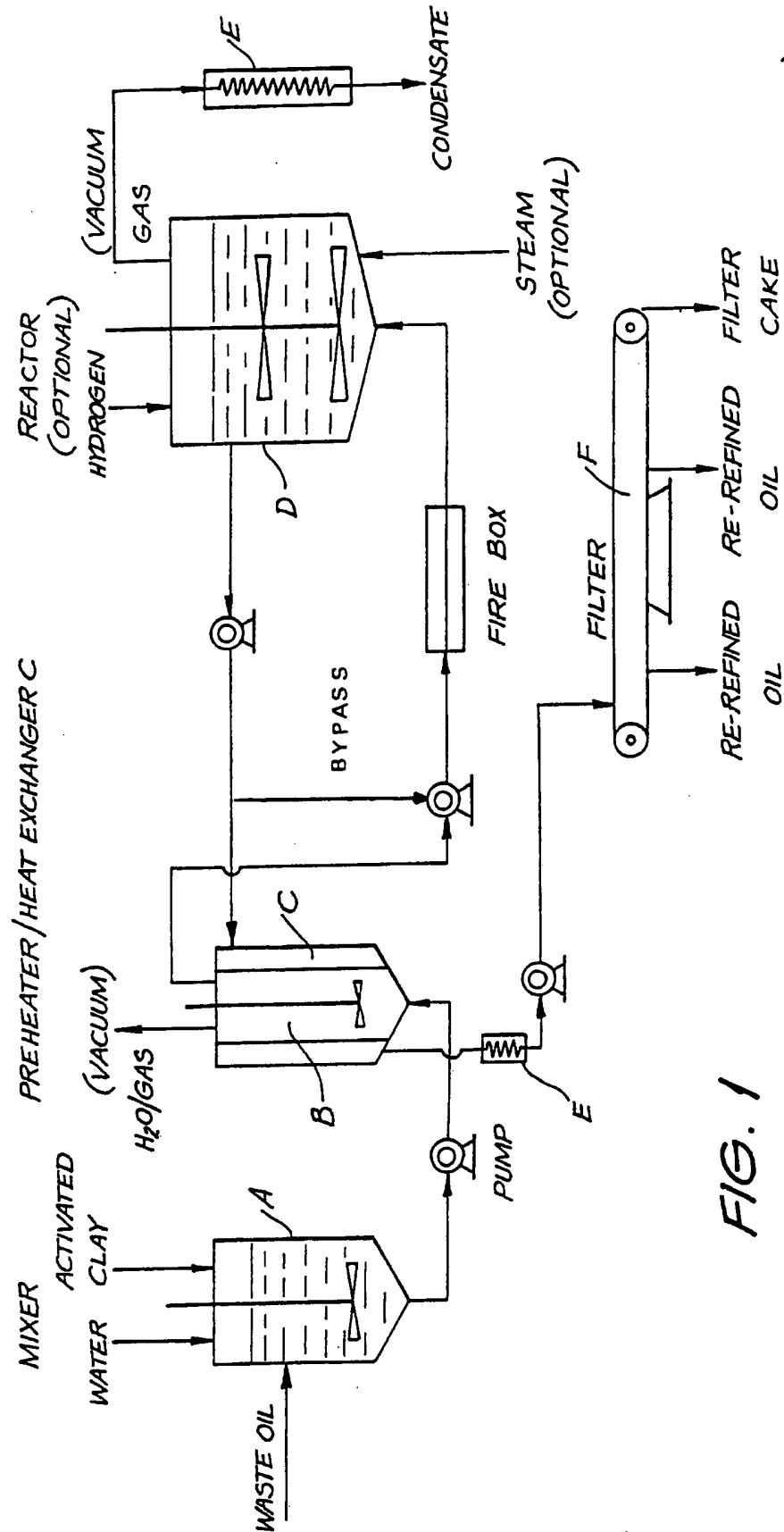
15 23. The additive according to any one of claims 18 to 20 wherein the inorganic compounds comprise magnesium sulfate, aluminium sulfate, sodium hydroxide and sodium hypochlorite in the proportion of 2:1:1:1.

24. The additive according to any one of claims 18 to 23 wherein the clay is a filter clay.

25. The additive according to claim 24 wherein the clay is acid activated.

20 26. The additive according to claim 25 wherein the clay is acid activated or acid activatable montmorillonite type bentonite.

27. Re-refined oil whenever produced by the process according to any one of claims 1 to 17.



1/1

FIG. 1

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent classification (IPC) or to both National Classification and IPC Int. Cl. ⁸ C10M 175/02, 125/30, C10G 25/00, 49/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	C10M 175/02, 125/30, 11/00, 1/10, C10G 25/00, 49/08	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
AU : IPC as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate of the relevant passages ¹²	Relevant to Claim No ¹³
X,Y	US,A,4502948 (TABLER) 5 March 1985 (05.03.85) See entire document	(18-20, 24-25) (1, 3-5, 8-9, 27)
X,Y	US,A,4411774 (JOHNSON) 25 October 1983 (25.10.83) See entire document	(18-20, 24-25) (1, 3-4, 8-9, 27)
X,Y	GB,A,1594879 (BORENSTEIN) 5 August 1981 (05.08.81) example 23	(18, 24-25) (1, 3, 8-9, 27)
X,Y	US,A,4151072 (NOWACK et al) 24 August 1979 (24.08.79) See entire document	(18-20, 24-25) (1, 3-5, 8-9, 27)
(continued)		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents :</p> <p>"A" Document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 27 July 1992 (27.07.92)		Date of Mailing of this International Search Report 6 Aug. 1992 (06.08.92)
International Searching Authority AUSTRALIAN PATENT OFFICE		Signature of Authorized Officer B. BOURKE <i>B Bourke</i>

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category*	Citation of Document, ¹¹ with indication, where appropriate of the relevant passages ¹²	Relevant to Claim No ¹³
X,Y	US,A,3098031 (HARRIS) 16 July 1963 (16.07.63) See entire document	(18, 24-25) (1, 3-5, 8-9, 27)
X,Y	GB,A,2099847 (PHILLIPS PETROLEUM COMPANY) 15 December 1982 (15.12.82) See entire document	(18-19, 24-25) (1,2,3-5,8-9,11,27)
X	GB, 228162 (DREYFUS) 19 January 1925 (19.01.25) claim 1	(18-19, 24)
Y	US,A,4383915 (JOHNSON) 17 May 1983 (17.05.83) See entire document	(1, 2, 3-5, 8-9,11 18, 24, 25, 27)